

Appendix 4-4. Evaluation of Chronic Toxicity Based Guidelines for Pesticides and Priority Pollutants in the Florida Everglades

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Introduction

The Everglades Forever Act (Section 373.4592(1)(a), Florida Statutes) passed by the Legislature found that “*the Everglades ecological system is endangered as a result of adverse changes in water quality, and in the quantity, distribution, and timing of flows, and, therefore, must be restored and protected.*” As a part of the Everglades Program, provided in the EFA (Section 373.4592(4)(e), F.S.) the Department and the South Florida Water Management District (SFWMD) are required to “*evaluate existing water quality standards applicable to the Everglades Protection Area and EAA canals.*” Furthermore, the Department is directed to use “the best available information to define relationships between waters discharged to, and the resulting water quality in, the Everglades Protection Area” (Section 373.4592(4)(e)3., F.S.). This document provides an evaluation of pesticides and priority pollutants which currently lack specific numeric water quality criteria. To this end, the Department has prepared this document which provides an evaluation of pesticides and priority pollutants in the EPA.

Evaluation of the ecological, toxicological or human health risks associated with many contemporary pesticides in the environment is limited due to a lack of numeric surface water criteria under Chapter 62-302, Florida Administrative Code. Previous reports have evaluated pesticides and priority pollutants, not currently listed in Chapter 62-302, F.A.C., based on detection frequencies (Gilbert and Feldman 1995; Bechtel *et al.*, 1999). Frequently detected compounds were typically identified as potential concerns and in need of further evaluation. Using this technique Bechtel *et al.*, (1999) reported that between 1992 and 1997, 22 pesticides were detected within the Everglades Protection Area. Several contemporary pesticides including atrazine, ametryn, hexazinone, bromacil, norflurazon and simazine were among the most frequently observed compounds (Bechtel *et al.*, 1999).

While the detection frequency approach provides useful information concerning pesticide use and movement, it is of limited utility in risk assessment. Some progress has been made towards integrating toxicological information into analyses of detected concentrations. Beginning in 1994, quarterly South Florida Water Management District (SFWMD) pesticide monitoring reports have included an assessment of potential human health and ecologic impacts. Currently the SFWMD assessment is based on Florida Ground Water Guidance Concentrations (FDEP, 1994), USEPA Criterion Maximum Concentrations (Section 304 (a), Clean Water Act), and aquatic toxicity data for select organisms (Pfeuffer, 1996). This procedure was utilized by Bechtel *et al.*, (2000) to evaluate pesticide detections in the Everglades Protection Area. To date, only detected

compounds have been evaluated in this manner including ametryn, atrazine, bromacil, diazinon, endosulfan sulfate, ethoprop, hexazinone, metolachlor, metribuzin, norflurazon and simazine, using toxicity information from a limited number of organisms (Pfeuffer 1999; Bechtel *et. al*, 2000). Despite the recent progress, a large information gap still exists, which limits our ability to effectively evaluate toxicological impacts to flora and fauna. A comprehensive review of all pesticides and priority pollutants currently monitored in the Everglades Protection and Everglades Agricultural Areas is needed to fill the gap.

Although Chapter 62-302 does not list specific numeric criteria for many contemporary compounds, it does provide narrative criteria and a means of numeric interpretation. Subsection 62-302.530(62), F.A.C. specifies that “substances in concentrations which injure, are chronically toxic to, or produce adverse physiological or behavioral response in humans, plants, or animals” shall not be present in surface waters of the state. Chronic toxicity is defined by Subsection 62-302.200(4), F.A.C. as “*the presence of one or more substances or characteristics or components of substances which: (a) are greater than one-twentieth (1/20) of the amount lethal to 50% of the test organisms in 96 hrs (96 hr LC₅₀) where the 96 hr LC₅₀ is the lowest value which has been determined for a species significant to the indigenous aquatic community; or (b) may reasonably be expected, based upon evaluation by generally accepted scientific methods, to produce effects equal to those of the substance specified in (a) above.*” Furthermore, surface waters of the State are to be free from components which “*are present in concentrations which are carcinogenic, mutagenic, or teratogenic to human beings or to significant, locally occurring, wildlife or aquatic species*” (Subparagraph 62-302.500(1)(a)5). The chronic toxicity standard was utilized to develop a set of guideline concentrations for the list of unregulated pesticides and priority pollutants currently monitored in the Everglades. The guidelines are meant to provide a basis for screening detected concentrations. If frequent or continued exceedances of the guideline concentrations are observed, further actions are warranted. Actions may include TMDL development, use of best management practices, and development of specific numeric criterion.

Methodology Used to Calculate Freshwater Guidelines Based on Chronic Toxicity and Human Health:

The SFWMD database was downloaded to FDEP on December 13, 1999. Based on Chemical Abstracts Service Registry Numbers (CASRN), the database contained 187 unique organic compounds of which only 48 currently have Class III standards. Synonyms were assigned based on information obtained from the EPA CASRN database (http://www.epa.gov/envirofw/html/emci/cas_registry_num.html), EPA IRIS (Integrated Risk Information System) database (<http://www.epa.gov/iris/subst/index.html>), and EPA ECOTOX database system (<http://www.epa.gov/ecotox/>). The parameter list was not limited to the current SFWMD analysis suite, rather all compounds analyzed since 1986 were included. The analysis suite has changed over the past 13 years in response to changing permit requirement, use patterns and detection (or non-detection) of specific compounds.

Freshwater criteria were taken from F.A.C. Chapter 62-777, *Contaminant Cleanup Target Levels*, which follow the requirements of F.A.C. Section 62-302.530 and Chapter 62-785, *Brownfields Cleanup Criteria Rule*. Toxicity criteria were established using the following protocol:

1. Select data with document codes of “C” or “M” from EPA Aquatic Toxicity Information Retrieval (AQUIRE) database available through ECOTOX (<http://www.epa.gov/ecotox/>) (Note: The documentation code indicates the type and completeness of method and result documentation accompanying the data. Documentation code “C” denotes a thorough methods and results documentation. Code “M” indicates that documentation is generally satisfactory, but one or more of the pieces of information are missing from either the methods or results section such as control information or chemical concentrations are unmeasured. Insufficient methods and results documentation are indicated by code “I”. Although a documentation code of “C” does not signify that these test data are better than test data receiving a documentation code of “I”, it does give ECOTOX users a means of determining the level of confidence associated with that test record. Appendix G of the ECOTOX Technical Support Document (http://www.epa.gov/ecotox/ecotox_tech_doc.htm) contains the scoring for each database.)
2. Take no action for substances for which insufficient data were retrieved to allow a reasonable choice of sensitive organisms;
3. Select only animal LC₅₀ data, except that plant data should be selected in the case of substances in which plant EC₅₀ values for growth or photosynthesis, or LC₅₀ values for biomass, are several orders of magnitude less than animal mortality LC₅₀ values.
4. Ignore data from salmonid fishes (salmon and freshwater trout);
5. Select the test and organism showing the greatest sensitivity to the toxicant. Extreme outliers should be ignored during this procedure, and several other types of data (such as data in which the endpoint or concentration had to be recalculated by EPA for entry into the database, and data based only on active ingredients) should also be removed from consideration if more clearly applicable data are available for sensitive organisms;
6. A factor of 5% (1/20) should be applied to the animal LC₅₀ data to generate a surface water cleanup target level. If a plant LC₅₀ or EC₅₀ value was chosen, then that value becomes the guideline, without the use of a factor;
7. Human health effects were calculated using the equations in **Figure 4-4-1**;
8. The guidance concentration for a parameter became the lower of human health or aquatic life chronic toxicity criteria. By protecting the most sensitive designated use all uses will be protected. The designated uses for Class III surface waters are “recreation, propagation and maintenance of a healthy well-balanced population of fish and wildlife” (Chapter 62-302.400(1), F.A.C).

Figure 4-4-1. Equations Used to Calculate Freshwater or Marine Surface Water Criteria Based on Human Health Endpoints.

For Non-Carcinogens:

$$\text{Water Criteria } (\mu\text{g/L}) = \frac{(RfD_{\text{oral}} \times BW)}{(FI \times BCF)} \times CF$$

For Carcinogens:

$$\text{Water Criteria } (\mu\text{g/L}) = \frac{(TR \times BW)}{(SF_{\text{oral}} \times [FI \times BCF])} \times CF$$

Parameter	Definition	Default Value
CF	Conversion factor ($\mu\text{g/mg}$)	1000
BW	Body weight (kg)	70 ^a
FI	Fish ingestion rate (kg/day)	0.0065 ^a
BCF	Bioconcentration factor (mg toxicant/kg fish per mg toxicant/L water)	Chemical-specific ^a
RfD _{oral}	Oral reference dose (mg/kg/day)	Chemical-specific ^b
SF _{oral}	Oral slope factor (mg/kg/day) ⁻¹	Chemical-specific ^b
TR	Target risk (unitless)	1 x 10 ⁻⁶

^aEquations, default parameters, and BCFs from *USEPA Technical Support Document for Water Quality-based Toxics Control*, EPA/505/2-90-001, 1991.

^bToxicity values from IRIS, HEAST, Region III RBC Tables, or other sources as provided in Appendix 4-IVA and 4-IVB: Sources and Derivation of Toxicity values used in Calculations.

Thirty four compounds found within the SFWMD database were not listed in Chapter 62-777. Toxicity guidelines for ten of these compounds (2-methyl-4,6-dinitrophenol, 2-nitrophenol, bis(2-chloroethoxy)methane, chloropicrin, delta-BHC, endosulfan sulfate, methiocarb, norflurazon, perthane, and tetradifon) were established using the aquatic toxicity portion of the previously discussed protocol (Appendix 4-IVC). Human health effects have not been evaluated for these ten compounds. Insufficient data are currently available to evaluate the remaining twenty four compounds.

Guideline Results

Guidance concentrations are presented in **Table 4-4-1**. Unless otherwise noted guideline values are the maximum not to be exceeded concentration.

Table 4-4-1. Pesticide and priority pollutant guidelines for the Everglades Protection Area. The entries “HH”, “TC”, and “NA” in the “Basis” column indicate that the guideline was derived from human health data, chronic toxicity data, or is currently unavailable, respectively.

Chemical Name	CASRN	Guideline (µg/L)	Basis
acenaphthene	83-32-9	3.0	TC
acephate	30560-19-1	190	TC
acrolein	107-02-08	0.4	TC
acrylonitrile	107-13-1	49.9	HH
alachlor	15972-60-8	0.596	HH
aldicarb	116-06-3	0.85	TC
aldicarb sulfone	1646-88-4	46	TC
aldicarb sulfoxide	1646-87-3	4.2	TC
ametryn	834-12-8	6.2	TC
anthracene	120-12-7	0.3	TC
atrazine	1912-24-9	1.8	HH
azobenzene	103-33-3	0.559	HH
benomyl	17804-35-2	0.3	TC
benzidine	92-87-5	NA	NA
BHC, alpha-	319-84-6	0.0116	HH
BHC, delta-*	319-86-8	79	TC
bis(2-chloroethoxy)methane*	111-19-1	9200	TC
bis(2-chloroethyl)ether	111-44-4	9.99	HH
bis(2-chloroisopropyl)ether	108-60-1	0.5	HH
bis(2-ethylhexyl)phthalate	117-81-7	0.02	HH
bromacil	314-40-9	97	TC
bromomethane (methyl bromide)	74-83-9	35	TC
bromophenyl phenyl ether, 4-	101-55-3	NA	NA
butylate	2008-41-5	10.5	TC
carbaryl	63-25-2	0.06	TC
carbofuran	1563-66-2	0.1	TC
carbophenothion	786-19-6	0.1	TC
chlorobenzene	108-90-7	17	TC
chloroethane (ethyl chloride)	75-00-3	NA	NA
chloroethylvinylether, 2-	110-75-8	NA	NA
chloro-m-cresol, p- (chloro-3-methyl phenol, 4-)	59-50-7	100	TC
chloronaphthalene, 2-	91-58-7	NA	NA
chlorophenol, 2-	95-57-8	130	TC
chlorophenylphenyl ether, 4-	7005-72-3	NA	NA
chloropicrin*	76-06-2	5.3	TC
chlorothalonil	1897-45-6	0.8	TC
chlorotoluene, o-	95-49-8	390	TC

Chemical Name	CASRN	Guideline (µg/L)	Basis
chlorpyrifos	2921-88-2	0.002	TC
chlorpyrifos ethyl	2921-88-2	0.002	TC
chlorpyrifos methyl	5598-13-0	0.035	TC
cis-1,3-dichloropropene (telone)	10061-01-5	NA	NA
cypermethrin	52315-07-8	0.0005	TC
DDD-P,P' (DDD,4,4)	72-54-8	0.003	HH
DDE-P,P' (DDE,4,4)	72-55-9	0.0006	HH
demeton	8065-48-3	1.35	TC
diazinon	333-41-5	0.0015	TC
dichlorobenzene, 1,2-	95-50-1	99	TC
dichlorobenzene, 1,2-	95-50-1	99	TC
dichlorobenzene, 1,3-	541-73-1	85	TC
dichlorobenzene, 1,3-	541-73-1	85	TC
dichlorobenzene, 1,4-	106-46-7	100	TC
dichlorobenzene, 1,4-	106-46-7	100	TC
dichlorobenzidine, 3,3'-	91-94-1	0.06	HH
dichloroethane, 1,1-	75-34-3	NA	NA
dichloroethene, 1,2- (mixture)	540-59-0	7000	TC
dichloroethene, cis-1,2-	156-59-2	NA	NA
dichloroethene, trans-1,2-	156-60-5	11000	TC
dichlorophenol, 2,4-	120-83-2	13	TC
dichlorophenoxy acetic acid, 2,4- (2,4-D)	94-75-7	80	TC
dichloropropane, 1,2-	78-87-5	2600	TC
dichloropropene, trans-1,3- (telone)	10061-02-6	NA	NA
dichlorprop (2,4-DP)	120-36-5	42	TC
dicofol (kelthane)	115-32-2	0.003	HH
diethylphthalate	84-66-2	380	TC
dimethoate	60-51-5	0.1	TC
dimethylphenol, 2,4-	105-67-9	261	HH
dimethylphthalate	131-11-3	1450	TC
di-n-butylphthalate	84-74-2	23	TC
dinitrophenol, 2,4-	51-28-5	3	TC
dinitrotoluene, 2,6-	606-20-2	4	HH
di-n-octylphthalate	117-84-0	NA	NA
diphenylhydrazine, 1,2-	122-66-7	0.38	HH
diquat	85-00-7	1.5	TC
disulfoton	298-04-4	0.3	TC
diuron	330-54-1	8	TC
EDC (dichloroethane, 1,2-)	107-06-2	5	HH
endosulfan sulfate*	1031-07-8	37.8	TC
endrin aldehyde	7421-93-4	NA	NA
ethion	563-12-2	0.007	TC
ethoprop	13194-48-4	0.315	TC
ethylbenzene	100-41-4	605	TC
ethylene thiourea (ETU)	96-45-7	1320	TC
fenamiphos	22224-92-6	0.225	TC
fluoranthene	206-44-0	0.3	TC

Chemical Name	CASRN	Guideline (µg/L)	Basis
fluorene	86-73-7	30	TC
fonofos	944-22-9	0.095	TC
glyphosate	1071-83-6	115	TC
heptachlor epoxide	1024-57-3	0.002	TC
hexachlorobenzene	118-74-1	0.00036	HH
hexachlorocyclopentadiene	77-47-4	2.95	TC
hexachloroethane	67-72-1	1.1	HH
hexazinone	51235-04-2	1020	HH
hydroxycarbofuran, 3-	16655-82-6	NA	NA
imidacloprid	13826-41-3	NA	NA
isophorone	78-59-1	645	TC
linuron	330-55-2	44.5	TC
metalaxyl	57837-19-1	36.5	TC
methamidophos	10265-92-6	0.000011	TC
methiocarb*	2032-65-7	0.25	TC
methomyl	16752-77-5	0.95	TC
methyl-4,6-dinitrophenol, 2-*	534-52-1	11.50	TC
methylene bromide	74-95-3	NA	NA
metolachlor	51218-45-2	1.08	TC
metribuzin	21087-64-9	64	TC
mevinphos	7786-34-7	0.0475	TC
monochrotophos	2157-98-4	NA	NA
naled	300-76-5	0.018	TC
naphthalene	91-20-3	26	TC
nitrobenzene	98-95-3	90	TC
nitrophenol, 2-*	88-75-5	1645	TC
nitrophenol, 4-	100-02-7	55	TC
nitroso-dimethylamine, N-	62-75-9	0.53	HH
nitroso-di-n-propylamine, N-	621-64-7	0.83	HH
nitroso-diphenylamine, N-	86-30-6	44	HH
norflurazon*	27314-13-2	815	TC
o,p'-DDD	53-19-0	NA	NA
o,p'-DDE	3424-82-6	NA	NA
o,p'-DDT	789-02-6	NA	NA
oxamyl	23135-22-0	8.5	TC
paraquat	1910-42-5	47	TC
parathion methyl	298-00-0	0.01	TC
permethrin	52645-53-1	0.001	TC
perthane*	72-56-0	1.0	TC
phenol	108-95-2	6.5	TC
phorate	298-02-2	0.0055	TC
prometryn	7287-19-6	21	TC
propham	122-42-9	500	TC
propoxur (baygon)	114-26-1	0.35	TC
pyrene	129-00-0	0.3	TC
ronnel	299-84-3	0.061	TC
simazine	122-34-9	5.8	HH

Chemical Name	CASRN	Guideline (µg/L)	Basis
tetradifon*	116-29-0	5.50	TC
toluene	108-88-3	475	TC
trichlorobenzene, 1,2,4-	120-82-1	22.5	TC
trichloroethane, 1,1,1-	71-55-6	270	TC
trichloroethane, 1,1,2-	79-00-5	28.5	HH
trichlorofluoromethane	75-69-4	NA	NA
trichlorophenol, 2,4,5- (2,4,5-T)	95-95-4	22.5	TC
trichlorophenoxy propionic acid, 2(2,4,5)- (silvex)	93-72-1	NA	NA
trifluralin	1582-09-8	0.78	HH
vinyl chloride	75-01-4	NA	NA
xylenes	1330-20-7	370	TC
zinc phosphide	1314-84-7	NA	NA

*No freshwater surface water criteria listed in Chapter 62-777, *Contaminant Cleanup Target Levels*.

HH = human health

NA = Not Available

TC = Toxicity Criteria, 1/20 of applicable LC₅₀ data

A comparison between calculated guidelines and typical method detection limits (MDL) and practical quantification limits (PQL) are presented in **Table 4-4-2**. It should be reiterated that the analytical procedures for many compounds have undergone significant improvement over the past two decades. Method detection limits and PQLs given in Table 4-IV-2 are the current standard values. Past values have been higher and the SFWMD's DBHYDRO database should be consulted for the MDLs of individual results. Where guidelines are greater than both the MDL and PQL risks can effectively be evaluated. Compounds with guidelines below the MDL cannot currently be evaluated based on toxicological risk, since concentration values above the guideline but below the MDL may not be detected; any measured concentration will automatically exceed the guidance concentration. These comparisons are meant to assist in the evaluation of current analytical methodology and provide guidance in their continued refinement.

Table 4-4-2. Comparison between guidelines and corresponding MDL and PQL as reported by FDEP Bureau of Laboratories, March 1999. Values of 0, 1 and 2 indicate that the guideline is greater than both MDL and PQL, between MDL and PQL, or less than both MDL and PQL, respectively. There are two entries for 1,2-, 1,3- and 1,4-dichlorobenzene. The higher MDL are achieved using w-bna (EPA 625) method while the lower MDL are obtained using w-voc (EPA 624) method. Several other compounds are listed twice with varied MDLs. The lower MDLs are obtained with improved methods, which are only performed at the request of SFWMD. Method detection limits and PQLs stated here are the current standard values, actual values vary due to a number of factors including sample volume, matrix interference and sediment content of water.

Chemical Name	Criteria	MDL	PQL	Comparison
acenaphthene	3	1.0	4.0	1
acephate	190	1.5	7.5	0
acrolein	0.4	10	40	2
acrylonitrile	49.9	4.0	16	0
alachlor	0.596	0.046	0.24	0
alachlor	0.596	0.3	1.5	1
aldicarb	0.85	2.0	5.0	2
aldicarb sulfone	46	2.0	5.0	0
aldicarb sulfoxide	4.2	2.0	5.0	1
ametryn	6.2	0.0093	0.049	0
ametryn	6.2	0.05	0.25	0
anthracene	0.3	1.0	4.0	2
atrazine	1.80	0.0093	0.049	0
atrazine	1.80	0.05	0.25	0
azobenzene	0.56	1.0	4.0	2
baygon (propoxur)	0.35	2.0	5.0	2
benomyl	0.3	2.0	4.0	2
BHC, alpha-	0.012	0.00093	0.0048	0
BHC, alpha-	0.012	0.01	0.05	1
BHC, delta-	79	0.00093	0.0048	0
BHC, delta-	79	0.01	0.05	0
bis(2-chloroethoxy)methane	9200	1.00	4.00	0
bis(2-chloroethyl)ether	9.99	1.00	4.00	0
bis(2-chloroisopropyl)ether	0.5	4.5	18	2
bis(2-ethylhexyl)phthalate	0.02	15	60	2
bromacil	97	0.037	0.19	0
bromacil	97	0.3	1.5	0
bromomethane	35	0.5	1.0	0
butylate	10.5	0.019	0.1	0
butylate	10.5	0.1	0.25	0
carbaryl	0.06	2.0	5.0	2
carbofuran	0.1	2.0	5.0	2
carbophenothion	0.10	0.028	0.029	0
carbophenothion	0.10	0.03	0.2	1
chloro-m-cresol, p-	100	1.0	4.0	0
chlorobenzene	17	0.5	1.0	0
chlorophenol, 2-	130	1.0	4.0	0
chlorothalonil	0.8	0.019	0.019	0

Chemical Name	Criteria	MDL	PQL	Comparison
chlorothalonil	0.8	0.02	0.2	0
chlorotoluene, o-	390	1.0	1.0	0
chlorpyrifos ethyl	0.002	0.019	0.1	2
chlorpyrifos ethyl	0.002	0.1	0.5	2
chlorpyrifos methyl	0.035	0.019	0.1	1
chlorpyrifos methyl	0.035	0.1	0.5	2
cypermethrin	0.0005	0.0046	0.048	2
cypermethrin	0.0005	0.005	0.05	2
DDD-P,P' (DDD,4,4)	0.003	0.0019	0.01	1
DDD-P,P' (DDD,4,4)	0.003	0.02	0.1	2
DDE-P,P' (DDE,4,4)	0.0006	0.0019	0.01	2
DDE-P,P' (DDE,4,4)	0.0006	0.02	0.1	2
demeton	1.35	0.093	0.49	0
diazinon	0.002	0.019	0.1	2
diazinon	0.002	0.1	0.25	2
dichlorobenzene, 1,2-	99	0.5	1.0	0
dichlorobenzene, 1,2-	99	1.0	4.0	0
dichlorobenzene, 1,3-	85	0.5	1.0	0
dichlorobenzene, 1,3-	85	1.0	4.0	0
dichlorobenzene, 1,4-	100	0.5	1.0	0
dichlorobenzene, 1,4-	100	1.0	4.0	0
dichlorobenzidine, 3,3'-	0.06	3	12	2
dichloroethene, 1,2- (mixture)	7000	0.5	1.0	0
dichloroethene, trans-1,2-	11000	0.5	1.0	0
dichlorophenol, 2,4-	13	1.0	4.0	0
dichlorophenoxy acetic acid, 2,4- (2,4-D)	80	2.0	4.0	0
dichloropropane, 1,2-	2600	0.5	1.0	0
dicofol/kelthane	0.003	0.019	0.038	2
dicofol/kelthane	0.003	0.02	0.4	2
diethylphthalate	380	1.0	4.0	0
dimethoate	0.10	1.0	5.0	2
dimethylphenol, 2,4-	261	3.0	12	0
dimethylphthalate	1450	1.0	4.0	0
di-n-butylphthalate	23	5.0	20	0
dinitrophenol, 2,4-	3.0	15	60	2
dinitrotoluene, 2,6-	4.0	1.0	4.0	0
diphenylhydrazine, 1,2-	0.38	0.94	3.8	2
diquat	1.5	1.0	5.0	1
disulfoton	0.3	0.028	0.15	0
diuron	8.0	0.4	0.8	0
EDC (dichloroethane, 1,2-)	5.0	0.5	1.0	0
endosulfan sulfate	37.8	0.0019	0.01	0
endosulfan sulfate	37.8	0.02	0.1	0
ethion	0.007	0.019	0.1	2
ethion	0.007	0.05	0.25	2
ethoprop	0.315	0.019	0.1	0
ethoprop	0.315	0.1	0.5	1
ethylbenzene	605	0.5	1.0	0

Chemical Name	Criteria	MDL	PQL	Comparison
ethylene thiourea (ETU)	1320	3.0	5.0	0
fenamiphos	0.225	0.028	0.15	0
fenamiphos	0.225	0.3	1.5	2
fluoranthene	0.3	1.0	4.0	2
fluorene	30	1.0	4.0	0
fonofos	0.095	0.019	0.1	1
fonofos	0.095	0.1	0.25	2
glyphosate	115	20	40	0
heptachlor epoxide	0.002	0.0093	0.48	2
heptachlor epoxide	0.002	0.01	0.1	2
hexachlorobenzene	0.00036	1.0	4.0	2
hexachlorocyclopentadiene	2.95	3.0	12	2
hexachloroethane	1.1	3.0	12	2
hexazinone	1020	0.019	0.1	0
isophorone	645	1	4.0	0
linuron	44.5	0.4	0.8	0
metalaxyl	36.5	0.056	0.29	0
metalaxyl	36.5	0.6	3	0
methamidophos	0.000011	1.0	5.0	2
methiocarb	0.25	2.0	5.0	2
methomyl	0.95	2.0	5.0	2
methyl-4,6-dinitrophenol, 2-	11.5	3.0	12	1
metolachlor	1.08	0.046	0.24	0
metolachlor	1.08	0.5	1.5	1
metribuzin	64	0.019	0.1	0
metribuzin	64	0.2	1.0	0
mevinphos	0.0475	0.037	0.19	1
mevinphos	0.0475	0.25	1.3	2
naled	0.018	0.074	0.39	2
naled	0.018	0.8	1.5	2
naphthalene	26	1.0	4.0	0
nitrobenzene	90	1.0	4.0	0
nitrophenol, 2-	1645	1.0	4.0	0
nitrophenol, 4-	55	4.0	16	0
nitroso-dimethylamine, N-	0.53	2.0	8.0	2
nitroso-di-n-propylamine, N-	0.83	1.0	4.0	2
nitroso-diphenylamine, N-	44.0	1.0	4.0	0
norflurazon	815	0.028	0.15	0
oxamyl	8.5	2.0	5.0	0
paraquat	47	1.0	5.0	0
parathion methyl	0.01	0.019	0.1	2
parathion methyl	0.01	0.1	0.5	2
permethrin	0.001	0.046	0.019	2
phenol	6.5	1.0	4.0	0
phorate	0.0055	0.029	0.15	2
phorate	0.0055	0.1	0.25	2
prometryn	21	0.019	0.1	0
prometryn	21	0.1	0.5	0

Chemical Name	Criteria	MDL	PQL	Comparison
pyrene	0.3	1.0	4.0	2
simazine	5.8	0.019	0.1	0
simazine	5.8	0.05	0.25	0
toluene	475	0.5	1.0	0
trichlorobenzene, 1,2,4-	22.5	1.0	4.0	0
trichloroethane, 1,1,1-	270	0.5	1.0	0
trichloroethane, 1,1,2-	28.5	0.5	1.0	0
trichlorophenol, 2,4,5- (2,4,5-T)	22.5	2.0	4.0	0
trifluralin	0.78	0.0093	0.01	0
trifluralin	0.78	0.02	0.1	0
xylenes	370	1.0	2.0	0
Greater than both MDL and PQL	Number	82		
	Percent Analytes	56.6		
Between MDL and PQL	Number	13		
	Percent Analytes	9.0		
Less than both MDL and PQL	Number	50		
	Percent Analytes	34.5		

Screening SFWMD Data Based on Toxicity Guidelines

Pesticide and priority pollutant results from 35 Everglades sites collected between February 1986 and April 1999 (**Figure 4-4-2**) were screened based on data qualifiers, blank contamination, and toxicity guidelines. Screening for fatal codes excluded 22 out of 131,679 samples based on qualification by a “J”, “N” or “Q”; no other fatal qualifiers were encountered. Data passing this test were evaluated for blank contamination. Equipment and field blanks were considered contaminated if the result was greater than the MDL (*i.e.*, the parameter was detected). All samples associated (*i.e.*, equivalent station, date and parameter) with contaminated blanks were eliminated. A total of 61 samples were disqualified based on blank contamination. The remaining data were evaluated relative to the toxicity guidelines or thresholds.

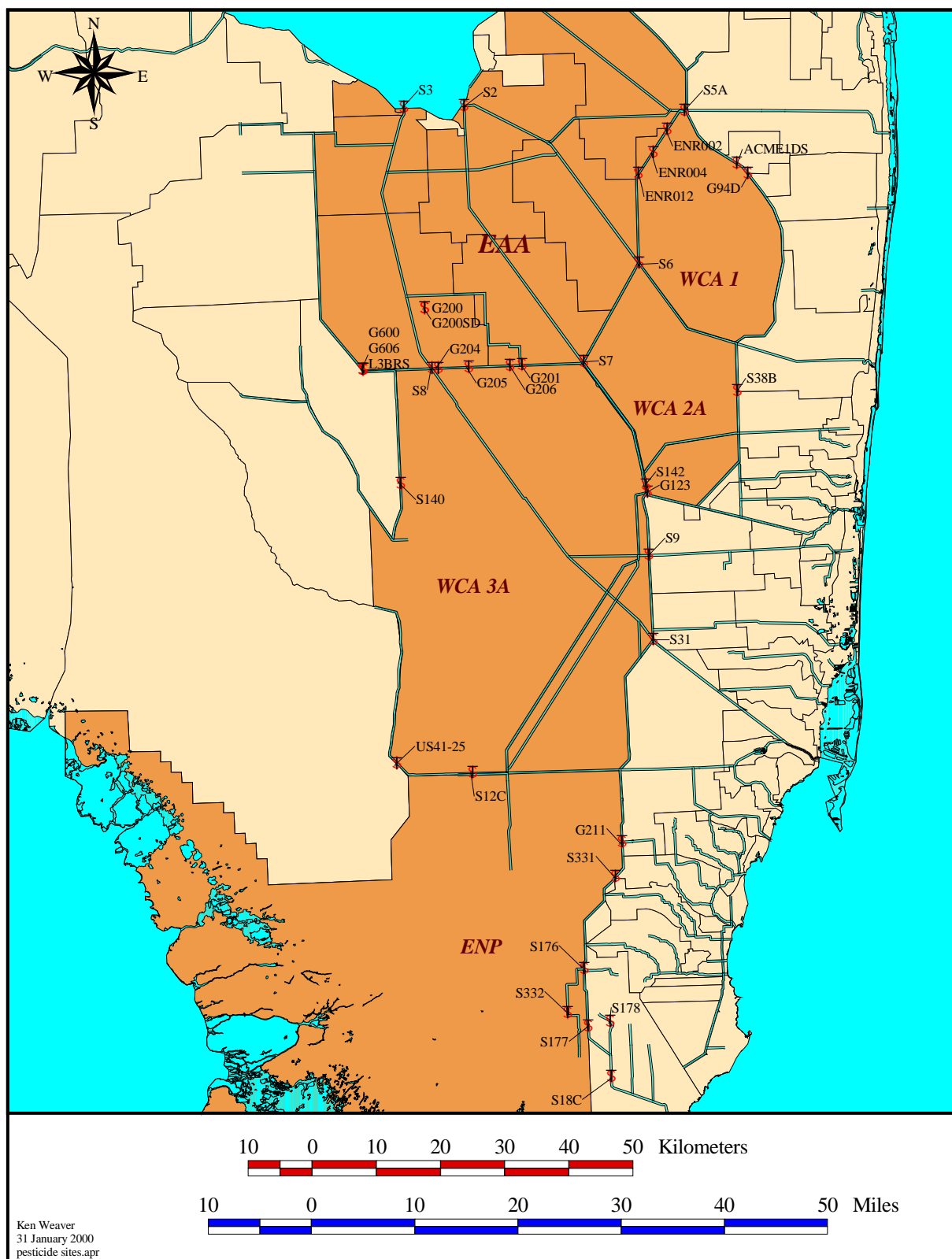
The threshold evaluation was performed by comparing toxicity guidelines to detected concentrations. Only values reported as greater than the MDL were considered detections. When a detected concentration exceeded the corresponding guideline, an excursion was recorded. For the purpose of excursion calculation, no value replacement was performed on results reported below the MDL. Additionally, replicate samples were not averaged as this would produce erroneous results for values below the MDL; instead the maximum replicate was used to represent the most protective concentration estimate. Data were summarized by station both annually and for the entire period of record based on detection and excursion frequencies. Using the total period of record excursion or detection frequencies, compounds were placed into three categories defined in Table 4-4-3. For compounds with guidelines, the evaluation was based on excursion rate. While compounds lacking guidelines were evaluated based on detection frequency.

Table 4-4-3. Definition of excursion categories used in the evaluation of Everglades Protection Area and Everglades Agricultural Area pesticide and priority pollutant data. Percent excursion and detection refer to the entire period of record for a given station.

Category	Evaluation	
	Compounds with Guidelines	Compounds without Guidelines
No Concern	No excursions	No detections
Potential Concern	> 0% and < 5% excursions	> 0% and < 5% detections
Concern	≥ 5% excursions	≥ 5% detections

The excursion categories are meant to provide some guidance in the interpretation of results. Use of the 5% break point between parameters classified as Potential Concerns and those identified as Concerns parallels the common scientific practice of allowing a 5% rejection limit in statistical analyses. Furthermore, the categories provide a means to rank the severity of excursions from water quality criteria and allow tracking of temporal and spatial trends.

Figure 4-4-2. SFWMD Everglades Pesticide Monitoring Network. Data are contained in the WRED database.



Atrazine

Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, and pineapple (Howard 1991). It has been detected in 51% of the samples from all 35 Everglades stations, since 1986. However, concentrations exceeding the guideline have occurred in only 51 out of 1089 samples (4.7%) at 14 stations (**Table 4-4-4**). The most frequent guideline excursions have occurred at the S5A, S6, S7 and S8 pumps and ENR inflow (ENR002). Based upon the 5% criterion atrazine is a compound of concern at the ENR002, G200, G200SD, G600, S38B, S5A, S6, S7 and S8 sites and a potential concern at S2, S176, S177, S178, and S332. Limited sample size and short periods of record at the S38B, G200 and G200SD stations restricts the evaluation and caution should be exercised in interpreting the results.

Median detected concentrations across all stations was 0.23 µg/L and ranged from 0.013 to 2.5 µg/L (**Table 4-4-5**). It should be noted that the summary statistics are biased high as values below the MDL were excluded due to an uncertain frequency distribution below the MDL. The true median is dependent upon not only the detected values but also the unknown distribution of values below the MDL. In order to provide an accurate summary of atrazine concentrations it is necessary to generate an estimate of the unknown frequency distribution. Below the MDL the frequency distribution is most likely bimodal with an unknown percentage at 0 µg/L and second population, which could be assumed to be normally distributed around some value below the MDL (*e.g.*, ½ MDL). The simplest estimate of the median is that it lies somewhere between two populations; one with all non-detected concentrations equal to zero and a second with all non-detected concentrations equal to the MDL. For example using 0 and MDL replacement for values less than the MDL yields median concentrations of 0.012 or 0.130 µg/L, respectively. The concentration summaries (**Table 4-4-5**), based solely upon detected concentrations, are therefore liberal estimates, perhaps by an order of magnitude.

Although atrazine was identified as a compound of concern for several stations in the northern EPA, its biologic/ecologic impacts are uncertain for a number of reasons. Given the low concentration estimates and infrequent guideline excursions, it appears that atrazine concentrations are tending to remain below ecologically significant levels with the exception of periodic pulses, which likely correspond to agricultural application (**Figure 4-4-3**). In fact the most sensitive organism from the toxicity literature (ECOTOX) is *Chlamydomonas reinhardtii*, which has an EC₅₀ of 19 µg/L; observed surface concentrations have remained below this threshold (**Table 4-4-5**). There is however a potential concern for human health effects. The human health based guideline is based upon assumptions of fish consumption rates and bioconcentration from a constant atrazine water concentration. These assumptions may not hold in the Everglades. At stations with adequate data, atrazine concentrations have been shown to remain below 1.8 µg/L over 50% of the time (**Table 4-4-5**). Rather than being a constant contaminant atrazine appears to be entering the system in pulses corresponding to periodic agricultural application. Furthermore, there is evidence that atrazine disappears rapidly from aquatic systems similar to the Everglades. The rate of hydrolysis of the herbicide is rapid under acidic or basic conditions, but not neutral, and is increased by the addition of humic materials in the sediment (Howard, 1991). Additionally, photo-

decomposition and volatilization occur under prolonged sunlight and high temperatures, conditions which are commonplace in South Florida. In fact, ENR and early STA 6 data commonly show a rapid reduction in atrazine concentrations and excursion frequencies between inflow (ENR002 and G600, respectively) and outflow (ENR012 and G606, respectively) structures in small areas relative to the conservation areas (**Table 4-4-4** and 4-IV-5). The proceeding argument, concerning hydrolysis assumes that degradation products are less toxic than the original compound. If the degradation products are more toxic than atrazine, then the process is detrimental.

Given the preceding arguments the true environmental fate of atrazine in the Everglades system is uncertain. A further review of major sources and sinks within the watershed is required to fully evaluate the risks associated with atrazine. Despite the uncertainty in atrazine impacts, it is advisable to develop mechanisms, such as best management practices (BMP) to reduce the occurrence of excursions. Additionally, given the ubiquitous nature of atrazine not only in the Everglades but also statewide, the development of a specific numeric criterion is desirable and recommended.

Table 4-4-4. Annual rate of atrazine excursions from guideline (1.8 µg/L). Annual rates are only listed for stations with excursions, while the total reflects all stations and years. In the Evaluation column a “C” or “PC” denote parameter of concern or potential concern at given station, respectively.

Station	Year	Percent Excursion (N)	Percent Detection (N)	Evaluation
ENR002	1996	25% (4)	100% (4)	C
ENR002	1997	25% (4)	100% (4)	
ENR002	1998	25% (4)	100% (4)	
G200	1998	100% (1)	100% (1)	C
G200SD	1998	100% (1)	100% (1)	C
G600	1998	33% (3)	100% (3)	C
S176	1991	14% (7)	29% (7)	PC
S177	1991	14% (7)	43% (7)	PC
S178	1988	25% (4)	25% (4)	PC
S2	1991	14% (7)	57% (7)	PC
S2	1994	17% (6)	83% (6)	
S332	1991	17% (6)	17% (6)	PC
S38B	1998	50% (4)	100% (4)	C
S5A	1987	33% (3)	33% (3)	C
S5A	1988	50% (4)	50% (4)	
S5A	1990	17% (6)	33% (6)	
S5A	1991	29% (7)	43% (7)	
S5A	1992	17% (6)	100% (6)	
S5A	1993	40% (5)	80% (5)	
S5A	1994	33% (6)	83% (6)	
S5A	1997	25% (4)	100% (4)	
S5A	1998	25% (4)	100% (4)	

Station	Year	Percent Excursion (N)	Percent Detection (N)	Evaluation
S6	1987	25% (4)	25% (4)	C
S6	1992	17% (6)	100% (6)	
S6	1993	40% (5)	100% (5)	
S6	1994	17% (6)	100% (6)	
S6	1996	25% (4)	100% (4)	
S6	1997	25% (4)	100% (4)	
S6	1998	25% (4)	100% (4)	
S7	1987	50% (4)	50% (4)	C
S7	1988	25% (4)	50% (4)	
S7	1992	20% (5)	100% (5)	
S7	1993	40% (5)	100% (5)	
S7	1994	17% (6)	83% (6)	
S7	1997	25% (4)	75% (4)	
S8	1992	33% (6)	83% (6)	C
S8	1993	20% (5)	80% (5)	
S8	1994	17% (6)	83% (6)	
S8	1995	25% (4)	100% (4)	
S8	1996	25% (4)	100% (4)	
S8	1997	40% (5)	100% (5)	
All Samples		4.7% (1089)	51% (1089)	

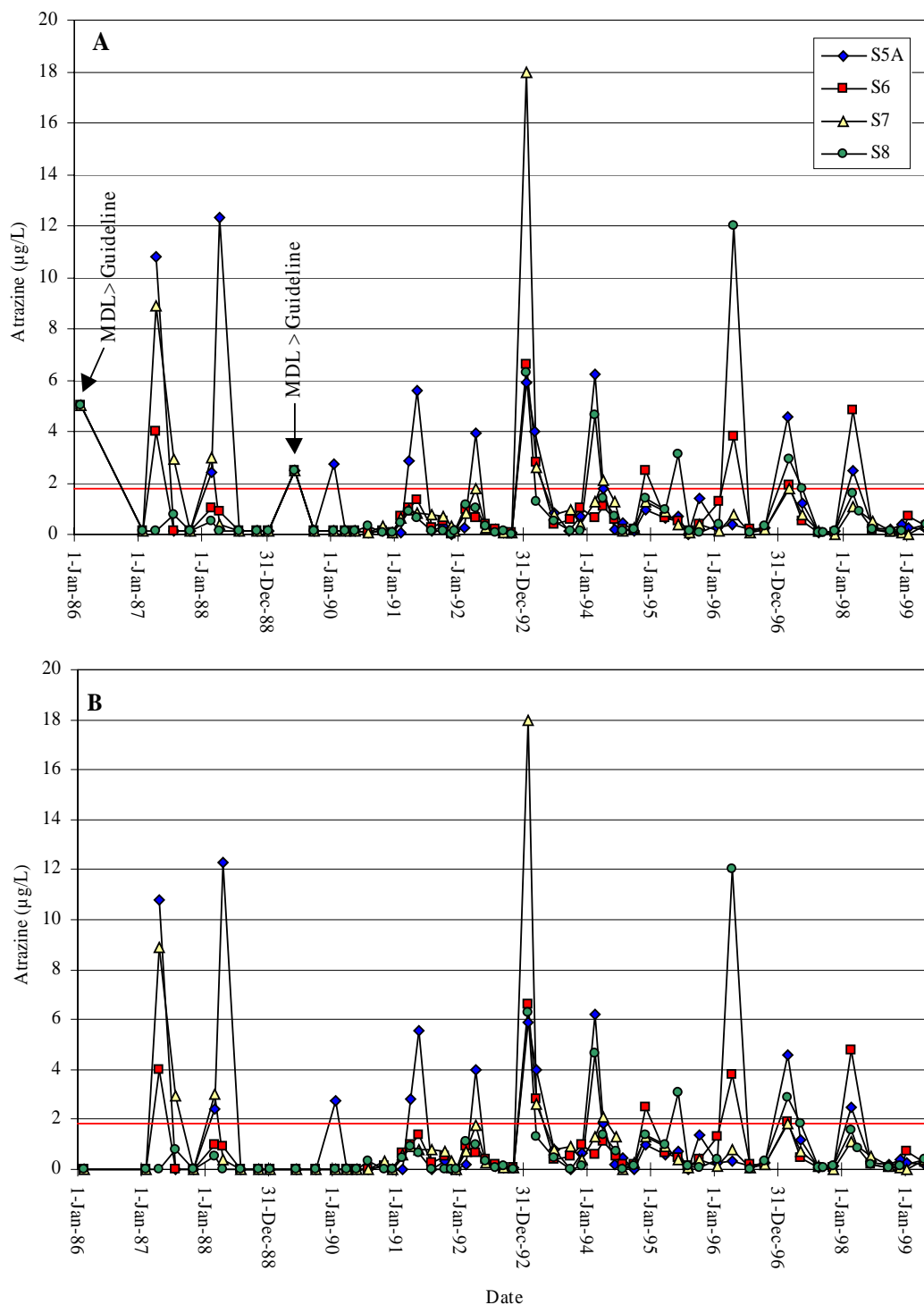
Table 4-4-5. Summary of atrazine concentrations ($\mu\text{g/L}$), February 1986 through April 1999. Replicate samples were averaged.

Site	Replacement with 0*	Replacement with the MDL [†]	Only Detected Concentrations					Detected N	Total N
	Median	Median	Median	First Quartile	Third Quartile	Min	Max		
ACME1DS	0.210	0.210	0.210	0.150	0.410	0.053	0.820	9	9
ENR002	0.268	0.268	0.268	0.171	1.475	0.115	2.900	20	20
ENR004	0.385	0.385	0.410	0.150	0.705	0.061	1.650	19	21
ENR012	0.110	0.110	0.340	0.128	0.475	0.061	1.300	13	21
G123	0.027	0.027	0.057	0.019	0.203	0.013	0.270	6	7
G200	2.322	2.322	2.322			0.043	4.600	2	2
G200SD	2.500	2.500	2.500			2.500	2.500	1	1
G201	0.443	0.447	0.885			0.885	0.885	1	2
G204	0.375	0.380	0.750			0.750	0.750	1	2
G205	0.065	0.070	0.130			0.130	0.130	1	2
G206	0.150	0.155	0.300			0.300	0.300	1	2
G211	0.006	0.011	0.040	0.014	0.085	0.012	0.093	4	8
G600	0.460	0.460	0.460	0.280	4.383	0.240	8.300	5	5
G606	0.295	0.295	0.295	0.155	0.395	0.040	0.465	5	5
G94D	0.180	0.180	0.180	0.105	0.370	0.016	0.710	10	10
L3BRS	0.000	0.100	0.170	0.043	0.430	0.011	1.700	25	57
S12C	0.000	0.091	0.047	0.020	0.215	0.012	1.370	20	58
S140	0.023	0.023	0.026	0.020	0.066	0.013	0.100	8	10
S142	0.120	0.120	0.120	0.035	0.370	0.025	0.490	9	9
S176	0.000	0.100	0.070	0.045	0.400	0.022	1.612	15	57
S177	0.000	0.100	0.087	0.037	0.253	0.016	1.820	18	57
S178	0.000	0.100	0.065	0.022	0.090	0.012	13.200	18	59
S18C	0.000	0.100	0.074	0.031	0.170	0.012	1.420	19	60
S2	0.150	0.170	0.355	0.160	0.708	0.061	4.130	38	59
S3	0.155	0.190	0.280	0.178	0.504	0.051	1.410	38	60
S31	0.000	0.100	0.170	0.056	0.425	0.014	1.500	25	59
S331	0.029	0.029	0.039	0.014	0.055	0.012	0.072	7	9
S332	0.000	0.100	0.037	0.019	0.281	0.014	3.690	14	57
S38B	1.300	1.300	1.300	0.868	1.875	0.470	2.100	6	6
S5A	0.225	0.260	0.430	0.210	2.625	0.021	12.300	41	58
S6	0.243	0.330	0.545	0.170	1.078	0.055	6.600	44	60
S7	0.335	0.380	0.691	0.250	1.300	0.022	18.000	43	59
S8	0.110	0.150	0.485	0.150	1.400	0.032	12.000	39	61
S9	0.000	0.100	0.090	0.024	0.130	0.002	0.250	19	59
US41-25	0.000	0.091	0.013	0.011	0.024	0.010	0.390	7	58
Combined	0.012	0.130	0.230	0.072	0.670	0.002	18.000	551	1089

*Values reported as less than the MDL were replaced with 0.

[†]Values reported as less than the MDL were replaced with the MDL. MDL values were assigned to individual results based on values given in the SFWMD database, rather than **Table 4-4-2**. The atrazine MDL ranged from 0.004 to 5.0 $\mu\text{g/L}$ with a median of 0.100 $\mu\text{g/L}$.

Figure 4-4-3. Atrazine concentrations at four stations classified as atrazine concern. Only the S5A, S6, S7 and S8 stations are depicted because they are the primary sources of atrazine excursions entering the EPA and an extended period of record is available. Figures 3A and 3B depict the upper and lower bond estimates for values below the MDL. Results less than the MDL were replaced with the MDL and 0 $\mu\text{g/L}$ in “A” and “B”, respectively. Replicate samples were averaged. The solid red horizontal line indicates the guideline (1.8 $\mu\text{g/L}$). Note: for two months (Feb. 1986 and June 1989) the MDL was elevated and above the guideline.



Other Compounds

In addition to atrazine only 15 compounds, including alachlor, alpha-BHC, bis(2-ethylhexyl)phthalate, carbofuran, chlorpyrifos ethyl, DDE-P,P', DDD-P,P', diazinon, dicofol, diquat, diuron, ethoprop, metolachlor, parathion methyl, and simazine, had recorded excursions. All other compounds are currently considered to be of no concern (**Table 4-4-6**). Only DDE-P,P', DDD-P,P', bis(2-ethylhexyl)phthalate, and diazinon meet the initial criteria to be classified as parameters of concern; the remaining twelve compounds were classified as potential concerns (Table 4-IV-6).

Table 4-4-6. Annual excursion rate from corresponding guideline for the time period 1986 through April 1999. Only stations and years with excursions are listed. In the Evaluation column a "C" or "PC" denote parameter of concern or potential concern at given station, respectively.

Chemical Name	Station	Year	Percent Excursion (N)	Percent Detection (N)	Evaluation
alachlor	L3BRS	1990	20% (5)	20% (5)	PC
alpha-BHC	S178	1990	17% (6)	17% (6)	PC
bis(2-ethylhexyl)phthalate	ENR002	1996	25% (4)	25% (4)	C
bis(2-ethylhexyl)phthalate	G200	1993	33% (3)	33% (3)	PC
bis(2-ethylhexyl)phthalate	G205	1993	25% (4)	25% (4)	PC
bis(2-ethylhexyl)phthalate	G206	1993	25% (4)	25% (4)	C
bis(2-ethylhexyl)phthalate	G206	1995	25% (4)	25% (4)	
bis(2-ethylhexyl)phthalate	S8	1993	25% (4)	25% (4)	PC
carbofuran	S31	1991	17% (6)	17% (6)	PC
chlorpyrifos ethyl	S6	1996	25% (4)	25% (4)	PC
DDD-P,P' (DDD,4,4)	G211	1999	50% (2)	50% (2)	C
DDE-P,P' (DDE,4,4)	ENR004	1998	20% (5)	20% (5)	PC
DDE-P,P' (DDE,4,4)	G211	1999	50% (2)	50% (2)	C
DDE-P,P' (DDE,4,4)	S5A	1995	25% (4)	25% (4)	C
DDE-P,P' (DDE,4,4)	S5A	1996	25% (4)	25% (4)	
DDE-P,P' (DDE,4,4)	S5A	1998	25% (4)	25% (4)	
diazinon	G94D	1997	25% (4)	25% (4)	C
diazinon	L3BRS	1998	25% (4)	25% (4)	PC
diazinon	S2	1995	25% (4)	25% (4)	PC
diazinon	S38B	1998	25% (4)	25% (4)	C
diazinon	S38B	1999	50% (2)	50% (2)	
dicofol	S18C	1992	14% (7)	14% (7)	PC
diquat	L3BRS	1994	20% (5)	20% (5)	PC
diuron	L3BRS	1992	17% (6)	17% (6)	PC
diuron	L3BRS	1995	25% (4)	25% (4)	
ethion	S178	1996	25% (4)	25% (4)	PC
ethoprop	S5A	1994	17% (6)	17% (6)	PC
metolachlor	S2	1993	20% (5)	20% (5)	PC
parathion methyl	S8	1995	25% (4)	25% (4)	PC
simazine	S6	1989	33% (3)	33% (3)	PC

DDT has been banned in the United States since 1972. Given the 28 year ban, the most likely source of DDT degradation products (DDD and DDE) is ecosystem recycling, primarily from the sediments. Excursions are more likely when sediments are disturbed in the watershed. Recent detections of DDE-P,P' and/or DDD-P,P' at the S5A and G211 stations may be associated with upstream construction projects or turbidity generated by water management carried out by the SFWMD and farmers. It should be noted that although total excursion rates for DDE-P,P' and DDD-P,P' at the G211 station are each 12.5% there was only one detection event (April 19, 1999) in less than two years of monitoring. This narrow period of record and small sample size limits analysis and can produce erroneous results. At this time it is uncertain whether this single event represents a true concern at G211.

Bis (2-ethylhexyl) phthalate is primarily used as a plasticizer in polyvinyl chloride (PVC) resins for fabricating flexible vinyl products. It is also used as replacement for PCB in electric capacitors and as an inert ingredient in many pesticide formulations. Excursions have occurred in 6.3% of the samples collected at G206 and 5% of the samples from ENR002. Potential sources for these excursions are uncertain. The source basins are largely agricultural, industrial sources are nonexistent. The only potential major source is the application of pesticide formulations containing bis (2-ethylhexyl) phthalate, but this is highly dependant upon the products used. There is also a potential for the compound to leach from PVC plastics in contact with the water, but this phenomenon would tend to be localized and short lived. Based on excursion rates the compound is currently considered a concern at these two stations. However, no excursions have occurred since 1996, at either station, suggesting it was a transitory event and the parameter's evaluation may soon be downgraded. Additionally, if a review of sources reveals that the major source of bis (2-ethylhexyl) phthalate excursions is plastic leaching then the compound may be deemed a non-concern.

Diazinon excursion rates at the S38B and G94D stations are currently 33% and 10%, respectively. These results suggesting that diazinon may be a concern in the North Springs Improvement District (S38B) and ACME Basin B (G94D). It should be noted that the diazinon guideline is below both the MDL and PQL (**Table 4-4-2**), therefore the magnitude of the "problem" remains uncertain as the actual excursion rates are potentially higher than stated here. Further uncertainty in the excursion rates is introduced by the fact that G94D and S38B were not monitored prior to 1997 and 1998, respectively. Given the uncertainties a thorough review of diazinon is warranted, including source and sink evaluation. The location of previous excursions provides some information on sources. Both the ACME Basin and North Springs Improvement District are largely urban basins. The contamination of urban basins by diazinon is not isolated to South Florida, but is a national trend (Gilliom *et al.*, 1999, Qian and Anderson 1999). Diazinon is widely used as an insecticide in home lawn and garden care and ranks 1st nationally among pesticides in home use (Gilliom *et al.*, 1999). However, this information is general and does not provide an adequate evaluation of sources. It would be useful to acquire data on usage patterns, including quantity and application time, and schedule monitoring around heavy use periods. This additional and focused monitoring would provide needed information on potential contamination pulses.

Compounds without Guidelines

Only 6 of the 24 compounds lacking criteria or toxicity guidelines have been detected in the study area (**Table 4-4-7**). Total detection rates in excess of 5% only occurred for trichlorofluoromethane and chloroethane. The remaining 4 detected compounds are classified as potential concerns. The lack of recent detections (for more than six years) of any parameters identified as potential concerns in **Table 4-4-7**, suggest that these should be downgraded to no concern.

Although trichlorofluoromethane was detected in 5 to 19% of the samples from ENR002, ENR012, G200, G200SD, G201, G204, G205, G206, and S8; it is unlikely that the compound is actually present at these stations. Trichlorofluoromethane, also called freon 11, has commonly been used as a refrigerant, fire extinguishing agent, foaming agent for polyurethane foams, degreaser and solvent, especially in the aerospace and electronics industries (Howard, 1990). Point sources, such as the aerospace and electronics industries, are non-existent in the EAA. There is potential for small episodic surface water contamination from refrigerant or fire extinguishing spills. However, trichlorofluoromethane is not persistent in surface waters, therefore detection of small random spills is unlikely. When released into surface water, trichlorofluoromethane is rapidly lost (half-life 4.3 hr. in a typical river), primarily to evaporation (Howard, 1990). It is more likely that samples were contaminated from leaky cooling systems during storage, transportation or laboratory analysis (Tim Fitzpatrick, personal communication). For these reasons it is most probable that the trichlorofluoromethane excursions were due to sample contamination and the compound should not be considered a parameter of concern.

Chloroethane was detected in one out of seven samples (14%) collected at the G94D station. At this time it is uncertain whether this single event represents a true concern at the G94D station.

Table 4-4-7. Annual detection frequency between 1986 and April 1999. Only detected compounds are listed. In the Evaluation column a “C”, “PC”, or “NC” denote parameters of concern, potential concern, or no concern at given station, respectively.

Chemical Name	Station	Year	Percent Detection (N)	Evaluation
chloroethane (ethyl chloride)	G94D	1997	33% (3)	C
di-n-octylphthalate	G200	1991	20% (5)	PC
di-n-octylphthalate	G204	1991	20% (5)	PC
monochrotophos	S6	1991	14% (7)	PC
trichlorofluoromethane	ENR002	1995	25% (4)	PC (NC)
trichlorofluoromethane	ENR012	1996	25% (4)	PC (NC)
trichlorofluoromethane	G200	1992	33% (3)	PC (NC)
trichlorofluoromethane	G200	1996	25% (4)	
trichlorofluoromethane	G200SD	1992	50% (4)	PC (NC)
trichlorofluoromethane	G200SD	1996	25% (4)	
trichlorofluoromethane	G201	1992	25% (4)	PC (NC)
trichlorofluoromethane	G201	1993	25% (4)	
trichlorofluoromethane	G201	1996	25% (4)	
trichlorofluoromethane	G204	1993	50% (4)	PC (NC)
trichlorofluoromethane	G204	1995	25% (4)	
trichlorofluoromethane	G204	1996	50% (4)	
trichlorofluoromethane	G205	1992	25% (4)	PC (NC)
trichlorofluoromethane	G205	1993	25% (4)	
trichlorofluoromethane	G205	1995	25% (4)	
trichlorofluoromethane	G205	1997	50% (2)	
trichlorofluoromethane	G206	1991	20% (5)	PC (NC)
trichlorofluoromethane	G206	1992	25% (4)	
trichlorofluoromethane	G206	1994	33% (3)	
trichlorofluoromethane	G206	1995	25% (4)	
trichlorofluoromethane	G206	1996	50% (4)	
trichlorofluoromethane	S8	1992	50% (4)	PC (NC)
trichlorofluoromethane	S8	1993	25% (4)	
trichlorofluoromethane	S8	1994	25% (4)	
trichlorophenoxy propionic acid, 2(2,4,5)-	S177	1987	25% (4)	PC
trichlorophenoxy propionic acid, 2(2,4,5)-	S3	1991	14% (7)	PC
trichlorophenoxy propionic acid, 2(2,4,5)-	S9	1991	14% (7)	PC
zinc phosphide	S6	1991	25% (4)	PC

Note: The evaluation for trichlorofluoromethane was altered from potential concern to no concern due to factors discussed in the text. This alteration is reflected by the “NC” code within parenthesis.

Summary

In order to define relationships between waters discharged to, and the resulting water quality in, the Everglades Protection Area, a means for evaluating deleterious impacts to flora and fauna from contaminants must be established. For a large number of parameters, deleterious impacts have already been quantified by state water quality criteria under Chapter 62-302, F.A.C. A criterion establishes a threshold above which the designated use will be effected. A violation of a criterion provides a presumption of violation of designated use. While specific criteria provide protection against a wide variety of contaminants, many contemporary pesticides and priority pollutants are not listed. To fill the analysis gap, thresholds need to be set for non-listed compounds. One approach to threshold development, supported by state law, is the calculation of chronic toxicity based on appropriate test organism LC₅₀ data. To be fully protective of the resource and its designated uses, potential human health effects must also be evaluated. The primary human health concerns for Class III surface waters are swimming and the maintenance of fish populations free from contaminate concentrations which pose unacceptable risks to human health. The risk associated with fish consumption is greater than swimming, due to bioconcentration in fish and faster gastrointestinal absorption (than dermal), therefore protection of consumptive uses will be protective of all designated human uses. It should be noted that toxicity based guidelines are not as rigorously developed as surface water quality criteria, but do fill a void in the absence of criteria. Review of monitoring data relative to the toxicity guidelines provides an initial step in the evaluation of the relationships between discharge waters and Everglades' water quality as it relates to unregulated (under Chapter 62-302, F.A.C.) synthetic organic compounds.

Based on a review of toxicity guidelines few monitored organic compounds are of concern in Everglades' surface waters. The compounds of greatest concern, atrazine, diazinon and DDT degradation products tend to be localized. Identification of stations where excessively contaminated (exceeding guideline) discharges occur provides information both on source location and potentially impacted areas. Diazinon excursions have been detected entering the eastern portion of WCA-1 and WCA-2A from the ACME Basin (G94D) and North Springs Improvement District (S38D), respectively. The magnitude and geographic extent of impacts from diazinon are difficult to gauge, at this time, due to a high MDL relative to the guideline. Atrazine concerns are primarily localized in the northern portion of the EPA occurring at pump stations between the EAA and Water Conservation Areas. Excursions tend to be periodic and are likely related to agricultural application in the EAA. Recent excursion at S38D suggest a concern in the east central portion of WCA-2A originating from the North Springs Improvement District. Degradation products of the persistent organochloride pesticide DDT continue to be a concern from the S-5A basin and possibly the Area B basin (G211).

Although the guidelines provide valuable information, they should not be applied without regard to contributory or mitigating factors. The guidelines are meant to provide an initial point of reference for potential impacts to flora and fauna. Where the guidelines suggest a concern, a more thorough analysis is necessary. As the analyses of atrazine and trichlorofluoromethane demonstrate, factors such as sample contamination, chemical

properties, and ecologic and environmental (*e.g.*, sunlight, temperature, pH) relationships can potentially alter the assumptions upon which the guidelines are based and thus affect the interpretation of monitoring data. Ultimately there is a need to verify any assumptions, which are called into question. In the cases of atrazine and diazinon, assumptions and conclusions can be verified through supplemental sediment and biological monitoring. Sediment samples provide information on the movement and persistence of compounds in the environment. South Florida Water Management District has, in the past, conducted sediment samplings. This program should continue and include internal marsh stations. Biologic monitoring (*e.g.*, fish, amphibians, reptiles) will provide vital information on the fate of compounds in the system. This type of monitoring is necessary to determine the extent that toxins are present in the food chain and is necessary to refine human health risks assessments. Furthermore, biomonitoring will assist in determining whether these compounds are bioconcentrating or degrading too rapidly to be of biological significance. A few fish surveys were conducted by the SFWMD and USGS in the early 1970's and 1995, respectively. The 1995 USGS study found detectable concentrations of chlordane, DDT, DDE-P,P', DDD-P,P', dieldrin, nonachlor and PCBs in largemouth bass (*Micropterus salmoides*) and Florida gar (*Lepisosteus platyrhincus*) (Haag and McPherson, 1997). However, many of the contemporary pesticides such as atrazine and diazinon, which are currently of greatest concern, were not analyzed.

Despite some uncertainty, there is currently sufficient evidence to warrant action on atrazine and diazinon. Actions should focus on reduction of occurrence and excursion frequencies. For atrazine the development of BMPs will potentially provide the necessary reductions. Current excursion data provide information on where to focus BMP efforts. Using these data along with information on landuse and application can be used to track the ultimate sources of contamination within the basins and further focus reduction efforts. Given the frequent detection frequency of atrazine not only in the Everglades but also statewide it is advisable to set specific numeric criterion for the compound on Chapter 62-302. Reduction of diazinon is a larger challenge given its use patterns. Urban sources are more difficult to track and less predictable (*e.g.* timing, quantity, location) than agricultural sources. Additionally, the diversity of urban landowners leads to significant difficulties in targeting educational and BMP programs to an audience of interested parties, no one program will suffice.

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